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Solar-driven carbon dioxide fixation using photosynthetic semiconductor bio-hybrids

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Solar-driven conversion of carbon dioxide to value-added carbon products is an ambitious objective of ongoing research efforts. However, high overpotential, low selectivity and poor CO₂ mass transfer plague purely inorganic electrocatalysts. In this instance, we can consider a class of biological organisms that have evolved to achieve CO₂ fixation. We can harness and combine the streamlined CO₂ fixation pathways of these whole organisms with the exceptional ability of semiconducting nanomaterials to harvest solar energy. A novel nanomaterial–biological interface has been pioneered in which light-capturing cadmium sulfide nanoparticles reside within individual organisms essentially powering biological CO₂ fixation by solar energy. In order to further develop the photosensitized organism platform, more biocompatible photosensitizers and cytoprotective strategies are required as well as elucidation of charge transfer mechanisms. Here, we discuss the ability of gold nanoclusters to photosensitize a model acetogen effectively and biocompatibly. Additionally, we present innovative materials including two-dimensional metal organic framework sheets and alginate hydrogels to shield photosensitized cells. Finally, we delve into original work using transient absorption spectroscopy to inform on charge transfer mechanisms.

Fossil fuel-derived energy has powered industrial development over the past two centuries. However, the exploitation of these energy reserves presents an indisputable complication, as these reserves are finite. Semiconductor-based devices have advanced to aptly capture inexhaustible solar energy in the form of electricity.¹ Although solar cells have been tested industrially at scale, they suffer from a persistent lack of adequate energy storage solutions.² Nature evolved to solve this issue in photosynthesis as organisms adapted metabolic pathways to reduce CO₂ and store solar energy in ensuing chemical bonds.³ The longevity and specificity of carbon fixation in biology is unrivalled by inorganic catalysts.⁴ Reaction specificity is established by enzymatic conformations that stabilize CO₂ reduction intermediates while steric hindrances assist in specific product

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formation.⁵ Furthermore, the genetic code ensures that this metabolism is exactly replicated. At the same time, however, engineered semiconducting materials outpace the light-harvesting ability of natural photosynthesis.⁶ For these reasons, combining light-absorbing materials with CO₂-reducing organisms offers an appealing solution for solar-based CO₂ fixation.^{4–6}

Progress has been made in coupling light harvesting devices with whole cell organisms to fix CO₂ into value-added chemicals.^{7,8} This work relies on the ability of electrotrophic bacteria to take up reducing equivalents from inorganic sources, including nanostructured electrodes.⁹ These organisms are commonly paired with a cathode in photoelectrochemical systems where they consume electrons to power the conversion of CO₂ into upgradeable carbon products. Exemplarily, acetogens receive reducing equivalents from solar harvesting electrodes and secrete acetate as a by-product of CO₂ fixation.⁷ While these efforts confirm the applicability of an integrated cell-semiconductor system, further improvement may be limited by the extracellular nature of the interface between the cell membrane and the electrode. For instance, it is important to increase the CO₂-reducing current while at the same time maintaining a stable interface between the cells and the cathode. However, increasing the CO₂-reducing current is hampered by the fact that high currents create a local basic environment around the proton-consuming cathode.⁷ The local basic environment irreparably damages the cell-semiconductor interface. Furthermore, extracellular electron uptake is not fully understood and therefore difficult to optimize. Although membrane-bound proteins take up electrons, a substantial part of these electrons may be lost due to the sluggish kinetics of charge transfer across the membrane.¹⁰ Collectively these limitations indicate that a paradigm shift is needed to redesign the interface between light-absorbing semiconductors and microorganisms.

In a landmark study, Sakimoto *et al.* confirm the ability to enhance acetogen *Moorella thermoacetica* (*M. thermoacetica*) with cadmium sulfide (CdS) nanoparticles.¹¹ The nanoparticles, which lie on the surface of the cell membrane, capture solar energy and supply reducing equivalents directly into the bacterium. The consumed reducing equivalents jump-start the cell metabolism, which is reliant on a source of electrons, and enable CO₂-to-acetate conversion *via* the Wood–Ljungdahl pathway (WLP).³ As this study marked the first report on a photosensitized microorganism for CO₂ reduction, further thorough elaboration and improvement is essential. Here, we discuss our studies that build on the first proof of concept. Briefly, we employ gold nanoclusters instead of cadmium sulfide as less cytotoxic and truly intracellular light harvesters. Secondly, we explore cytoprotective materials to shield bacteria from photooxidation due to harsh light and reactive oxygen species (ROS). Finally, we make inroads in elucidating the charge transfer mechanism at the biologic–inorganic interface using transient absorption spectroscopy.

Sakimoto and coworkers report on the first successful study to incorporate light-absorbing nanoparticles within acetogenic bacteria to enable CO₂-to-acetate conversion.¹¹ *M. thermoacetica* induces the precipitation of CdS nanoparticles with the addition of Cd²⁺ and a source of sulfur such as cysteine. Through an enzymatic process, the sulfur is reduced to sulfide and readily reacts with Cd²⁺ to form high quality CdS nanoparticles [Fig. 1(a)]. These nanoparticles are primarily anchored on the membrane of *M. thermoacetica* [Fig. 1(b)]. Upon illumination, the CdS nanoparticles deliver photogenerated electrons to metabolic pathways that

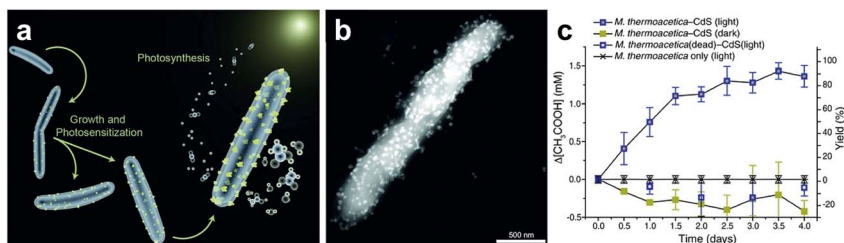


Fig. 1 (a) Model *M. thermoacetica*-CdS construct illustrating early growth stage, CdS nanoparticle ripening (yellow) and CO₂ reduction into acetate. (b) STEM image of *M. thermoacetica*-CdS hybrid. (c) Acetate obtained from *M. thermoacetica*-CdS during photosynthesis with deletional controls. Reproduced with permission.¹¹ Copyright 2016 The American Association for the Advancement of Science.

realize CO₂ reduction and secrete exogenous acetate [Fig. 1(c)]. Further cysteine is added to serve as a hole scavenger to improve charge separation at the nanoparticle interface. The discovery of photosensitized microorganisms for CO₂ fixation effectively sets up a novel line of investigation. It conceptualizes a new interface between whole microorganisms and semiconductors while confirming light-induced intracellular charge transfer in non-photosynthetic microorganisms. While photosensitized microorganisms enable the photoreduction of CO₂, they also present opportunities for investigating the interface between nanomaterials and whole-cell organisms. Electron transfer without added or produced molecular mediators, such as H₂, viologens or membrane-bound proteins, spurs questions on whether we can inject electrons at various points in biologic charge transport chains. For example, if light-activated nanomaterials jump-start CO₂ reducing pathways, could we potentially target more specific parts of the cell metabolism by material design? Additionally, could we use the light-controlled nanomaterials to set up studies to explore how organisms take up electrons? Applications beyond CO₂ fixation of photosensitized whole-cells merit more in depth discussion.

Furthermore, CdS nanoparticles, while effective light absorbers, pose a known environmental hazard and are acutely cytotoxic to bacteria as they induce oxidative stress.¹² Moreover, a more effective system could be realized with intracellular particles that permeate the whole cell instead of mostly just the membrane.

Gold nanoclusters (AuNCs) are sub-nanometric particles that consist of several gold atoms bound together into a network by ligands such as glutathione. At this level of confined atomicity, AuNCs harbor chromophore-like discrete energy states.¹³ Therefore, the clusters act as viable light harvesting centers. Additionally, through synthetic manipulation, their core size may be tuned to optimize for passage through the cell membrane thus enabling intracellular localization of the clusters.¹⁴ Interchangeable surface ligands also enable exquisite control over the biochemical properties of the cluster. Au₂₂(SG)₁₈ (SG is glutathione), a type of AuNC, offers water solubility and high fluorescence,¹⁵ a marker for light harvesting, establishing it a prime candidate for microorganism photosensitization¹⁶ [Fig. 2(a)].

Studies have previously confirmed that cells take up AuNCs with high efficiency and low cytotoxicity, as gold and glutathione are individually

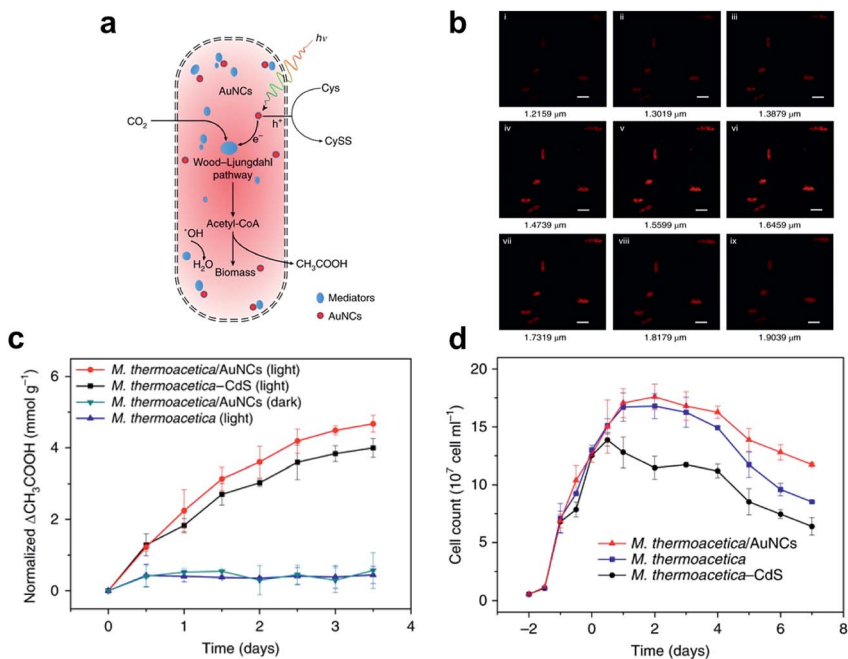


Fig. 2 (a) Schematic of *M. thermoacetica*- $\text{Au}_{22}(\text{SG})_{18}$ highlighting pathways to obtain acetate from solar energy. (b) Structure illumination microscopy (SIM) images at different focal planes with emission at 540 nm from $\text{Au}_{22}(\text{SG})_{18}$ in *M. thermoacetica*. (c) Normalized acetate production from *M. thermoacetica*-nanoparticle constructs in continuous photosynthesis. (d) Cell counts from *M. thermoacetica*-nanoparticle cultures. Reproduced with permission.¹⁶ Copyright 2018 Nature Publishing Group.

biocompatible.¹⁷ $\text{Au}_{22}(\text{SG})_{18}$ specifically, when added to a pre-exponential culture of *M. thermoacetica*, is taken up with over 90% efficiency and remains stable over a period of at least seven days.¹⁶ We have found $\sim 4 \times 10^{-7}$ mg of $\text{Au}_{22}(\text{SG})_{18}$ per cell to be an optimal concentration for our experiments. Furthermore, $\text{Au}_{22}(\text{SG})_{18}$ does not inhibit growth or other primary cell functions of *M. thermoacetica* at optimal concentrations. In fact, cell numbers and colony-forming units are higher in cultures of *M. thermoacetica*- $\text{Au}_{22}(\text{SG})_{18}$ than in *M. thermoacetica*-CdS [Fig. 2(d)]. Advantageously, it has been determined that certain conformations of AuNCs quench radicals, including ROS.¹⁸ In photosensitized bacteria, ROS is created as a toxic by-product upon photo-activation of the nanoparticles.¹⁹ This effect is particularly destructive with CdS. Results show that during photosynthesis the level of intracellular ROS is much lower in *M. thermoacetica*- $\text{Au}_{22}(\text{SG})_{18}$ as compared with *M. thermoacetica*-CdS. Altogether, these metrics of improved cell culture viability indicate that CO_2 -to-acetate yield may be higher in *M. thermoacetica*- $\text{Au}_{22}(\text{SG})_{18}$ constructs.

As hypothesized, $\text{Au}_{22}(\text{SG})_{18}$ nanoclusters permeate the entire cellular structure and are found localized beyond the cell membrane.¹⁶ Structure illumination microscopy is employed to resolve the placement of AuNCs in the cells by detecting fluorescence from the AuNCs under excitation at 540 nm. Fig. 2(b) shows fluorescence emission emanating quasi-uniformly in the cells. Images of

AuNCs in *M. thermoacetica* at a series of focal planes demonstrate that AuNCs can indubitably be found throughout the cells. Critically, the improved cell viability and intracellular penetration through the application of Au₂₂(SG)₁₈ as a photosensitizer lead to higher rate of acetic acid production [Fig. 2(c)]. After a period of four days of constant photosynthesis, the yield of acetic acid in the *M. thermoacetica*-Au₂₂(SG)₁₈ culture is appreciably higher than in the *M. thermoacetica*-CdS construct.¹⁶ Ultimately, AuNCs function as a powerful second-generation photosensitizer. Additional consideration is needed to elucidate the transport mechanism of Au₂₂(SG)₁₈ into the cytoplasm, as well as the role of individual charge uptake pathways within the cell.

AuNCs are effective photosensitizers in bacteria for solar-driven CO₂ fixation. While the rate of photooxidation is diminished with the use of AuNCs, it still persists in the system as a whole. Non-photosynthetic bacteria such as *M. thermoacetica* are not evolved to handle the high photon flux required for successful photosynthesis. Furthermore, cysteine, which acts as the hole scavenger in both CdS and AuNC systems, becomes depleted and currently limits the total output of acetic acid.^{11,16} A strategy has been developed in which cystine is reduced back to cysteine by photoactive TiO₂ nanocatalysts.²⁰ Although the photoreduction of cystine increases the availability of cysteine, which allows for a higher acetate yield, it comes at the expense of much higher photooxidation in the system. The TiO₂ nanocatalysts are responsible for photoanodic water oxidation that produces O₂ and toxic amounts of ROS.^{19,21} For these reasons, it is necessary to identify cytoprotective materials that will shield the photosensitized bacteria from photooxidative damage.

Advantageously, the cysteine/cystine redox shuttle allows for physical segregation of the photosensitized bacteria and the TiO₂ nanocatalysts. A selective membrane that quenches ROS and restricts O₂ passage while maintaining the diffusion of CO₂ and the redox shuttle would be beneficial. Photosynthetic microorganisms such as cyanobacteria emit extracellular polymers that contain UV-blocking molecules.^{22,23} Additionally, a plethora of robust microbes resist changes in temperature, pH, and salinity by forming spores.²⁴ Diatoms, for instance, synthesize siliceous exoskeletons to protect themselves from environmental stressors. Taking a cue from nature, encapsulation of the photosensitized bacteria would improve their ability to withstand harsh circumstances.²⁵

Hydrogels, including alginate, are commonly employed to encapsulate a unit of cells as they allow for unencumbered proliferation. Bacteria grow without restriction as they form microvoids in the soft alginate hydrogel.²⁶ This offers the advantage that bacteria would not lose their protection as they replicate, and dormant states are not induced by otherwise tight armor.²⁷ Fig. 3(a) demonstrates the growth of *M. thermoacetica* inside of alginate microspheres produced by a microfluidic injection process (see Experimental section below). *M. thermoacetica* creates microvoids inside of the alginate microspheres as determined by environmental scanning electron microscopy. Moreover, as alginate primarily consists of water, its CO₂ diffusive properties are the same as those of the aqueous culture media. The viability of *M. thermoacetica* decreases over the duration of whole photosynthesis with CO₂ reduction coupled with O₂ evolution. This is due to the strict anaerobic nature of *M. thermoacetica*, as it does not have a protective mechanism against O₂ or ROS. The alginate scavenges and attenuates the concentration of superoxides, hypochlorites and peroxides. This leads to an

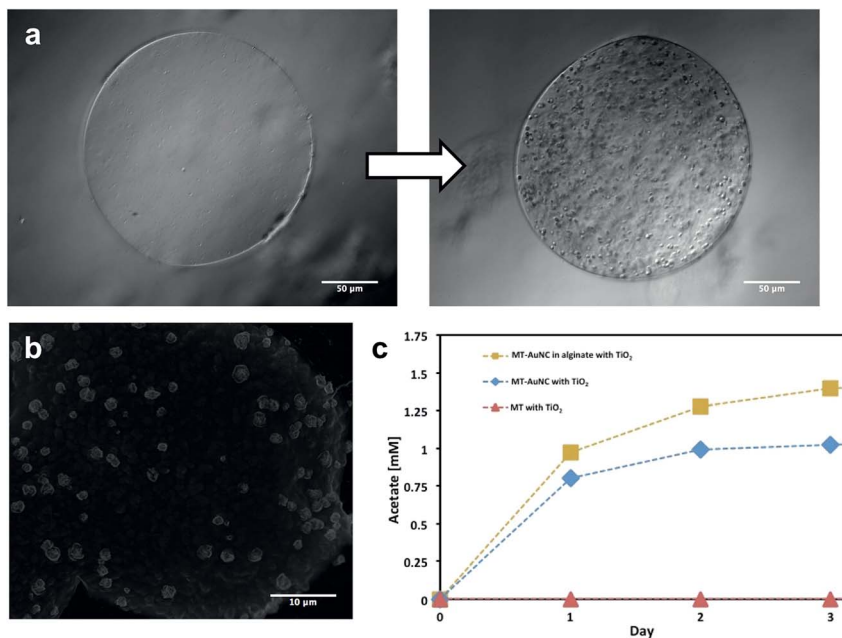


Fig. 3 (a) Differential interference contrast microscopy illustrates *M. thermoacetica* growth from day 0 to day 4 encapsulated in alginate microspheres. (b) Environmental scanning electron microscopy image shows detailed microvoids of an alginate sphere populated with *M. thermoacetica*. (c) CO₂-to-acetate production by encapsulated photosensitized *M. thermoacetica* with light-activated TiO₂ nanoparticles to reduce cystine to cysteine molecular redox shuttle.

increase in acetate during photosynthesis by *M. thermoacetica* [Fig. 3(c)]. A further protective layer may be synthesized on the surface of the bacteria-filled hydrogel.²⁸ For example, polydopamine and silica have been patterned directly on the surface of alginate to shield cells from stresses.²⁹

Metal organic framework (MOF) materials have received consideration as cytoprotective materials that are directly crystallized on or wrap around biological structures.^{30,31} Our group has developed a strategy to uniformly wrap photosensitized *M. thermoacetica* with a nanometric thick MOF monolayer for cytoprotection.³² The MOF monolayer maintains a dynamic wrapping during cell elongation, separation and even of newly grown cell surfaces [Fig. 4(a)]. Importantly, *M. thermoacetica* covered with the MOF monolayer sustains a smaller drop in viability under increasing concentrations of a model ROS, H₂O₂, as compared to the bare *M. thermoacetica* [Fig. 4(c)–(e)]. The viability is enhanced due to the catalytic activity of the MOF enclosure toward decomposition of the ROS. The MOF monolayer contains a zirconium cluster, which like zirconia particles rapidly decomposes H₂O₂ [Fig. 4(b)]. The MOF-wrapped *M. thermoacetica*–Au₂₂(SG)₁₈ can continuously produce acetate from CO₂ reduction under oxidative stress. MOF-wrapped photosensitized *M. thermoacetica* was shown to produce up to 200% more acetate than its bare counterpart under whole photosynthesis conditions. Therefore, the MOF cytoprotective method addresses the inherent vulnerability of anaerobes to oxidative stress, and provides a suitable platform for implementing

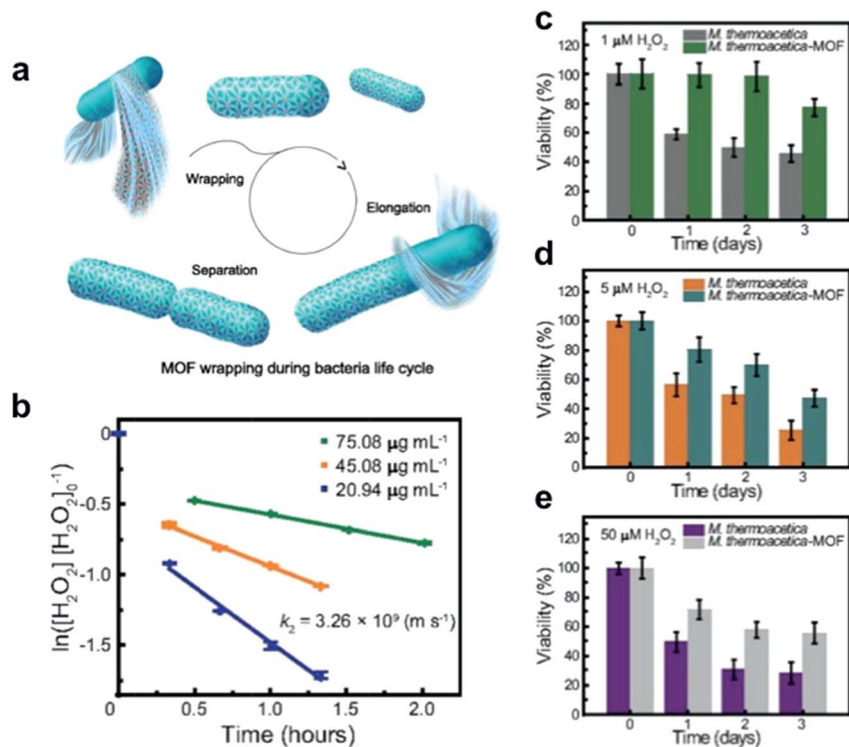


Fig. 4 (a) Depiction of spontaneous zirconium-based MOF-wrapping of *M. thermoacetica* by bonding to membrane-linked phosphate units. (b) Hydrogen peroxide decomposition by zirconium-based MOF. (c)–(e) Enhancement of viability of MOF-wrapped *M. thermoacetica* compared to bare *M. thermoacetica* at various hydrogen peroxide concentrations. This figure reproduced with permission.³² Copyright 2018 the National Academy of Sciences of the United States of America.

a whole artificial photosynthesis with both carbon dioxide reduction and oxygen evolution reaction.

A final aspect of the photosensitized microorganism system that is worth exploring is the mechanism of electron transfer between the inorganic light harvesting nanoparticles and the cell. While electron transfer processes between a poised electrode and electrotrophic bacteria have been investigated, those studies are limited by the inability to replicate and observe the processes *in situ* by spectroscopic means.³³ Photosensitized bacteria lend themselves as a platform to undertake transmittance-based transient absorption (TA) spectroscopy to study charge carrier lifetimes, as these colloidal suspensions are translucent and modular.³⁴ By applying controls the molecular basis of charge uptake can be inferred. The biochemical activity of proteins confirmed to take up reducing equivalents can be correlated with the results obtained with TA. In the event of hydrogenase involvement, the photoexcited electrons would help generate H_2 , which is then used in the WLP to convert CO_2 into acetate whereas the direct uptake of those electrons by membrane-bound proteins including cytochromes, ferredoxins and flavoproteins would facilitate ATP synthesis³⁵ [Fig. 5(a)]. In the first of its kind study, Kornienko and colleagues subjected *M. thermoacetica*-CdS

constructs to hydrogen incubation pre-photosynthesis at varying lengths of time in order to ramp up hydrogenase activity.³⁴ The rate of acetate production is highest in the first three hours for those samples with no hydrogen incubation but the average rate of acetate activity over 48 hours is highest in the samples with the longest hydrogen incubation. While seemingly paradoxical, the results suggest that two electron uptake processes take place. In samples with limited hydrogenase activity, the electrons feed directly into membrane bound proteins accelerating acetate production but ultimately cannot sustain metabolic activity due to a lack of high energy reducing equivalents [H_2 , $NAD(P)H$, Fd]. Whereas samples with sufficient hydrogenase activity, a CdS-to-hydrogenase electron transfer pathway is established to produce high energy reducing equivalents. Accordingly, TA kinetic results demonstrate faster decay kinetics in *M. thermoacetica*-CdS hybrids after hydrogen incubation than in *M. thermoacetica*-CdS grown with glucose and bare CdS [Fig. 5(b)]. These observations support the notion of electron transfer to an acceptor site on hydrogenase.

Moreover, due to the direct intracellular interface formed in *M. thermoacetica*- $Au_{22}(SG)_{18}$, this hybrid system could provide more insight into electron transfer processes. Strong quantum confinement effects and single electron transitions in AuNCs are manifested in their physicochemical properties such as discrete energy levels, multiple absorption bands and enhanced photoluminescence.³⁶ However, insufficient progress has been made in uncovering photoelectron transfer mechanisms. More efforts are needed to fully understand AuNCs excited state interactions, especially for energy conversions. We have established a model system as our starting point to elucidate the electron-donating ability of $Au_{22}(SG)_{18}$ to methyl viologen (MV^{2+}). The stability of its radical cation (MV^{+}) and the ease of its spectroscopic detection makes MV^{2+} favorable for fundamental studies.³⁷ TA allows for the spectroscopic determination of electron-transfer yield and associated kinetics of charge transfer in reduced methyl viologen with a characteristic absorption at 600 nm and 390 nm. More controlled experiments could provide new insights in understanding the intracellular photoexcited electron transfer process.

Altogether, photosensitized microorganisms offer a pioneering approach to convert CO_2 to upgradeable hydrocarbons using solar energy. This biohybrid

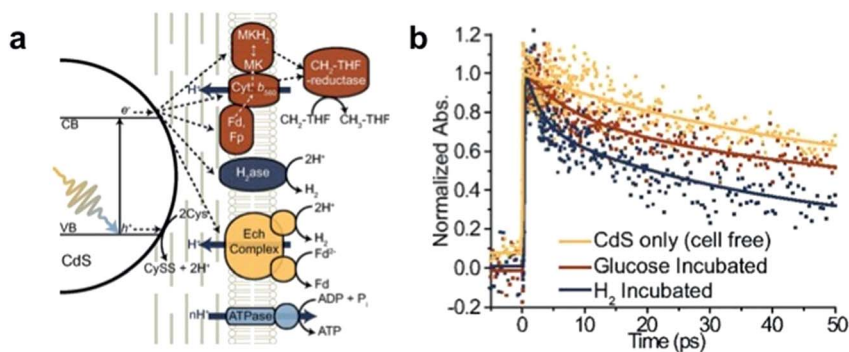


Fig. 5 (a) Schematic featuring possible active photoelectron uptake mechanisms. (b) Transient absorption plot of bare CdS, glucose and H_2 incubated *M. thermoacetica*-CdS. Fig. 5(a) and (b) reproduced with permission.³⁴ Copyright 2016 the National Academy of Sciences of the United States of America.

approach exploits the replication, self-healing and specificity of CO₂-fixing whole bacteria and the extraordinary solar capture of semiconducting nanoparticles. The intracellular interface, particularly in the AuNC constructs, circumvents the sluggish kinetics associated with extracellular charge uptake. Progress in cyto-protective materials will enable the application of this technology. Additionally, understanding gained through spectroscopic studies will shape future iterations of photosensitizers as well as optimize the pairing process. Finally, we hope engaged readership and research will be drawn to our highlighted areas of active investigation.

Experimental

AuNCs synthesis, *Moorella thermoacetica* growth and photosensitization

Red-emitting Au₂₂(SG)₁₈ synthesis is outlined by Zhang and coworkers.¹⁶ Solutions of HAuCl₄ (12.5 mL, 20 mM) and glutathione (7.5 mL, 50 mM) were combined into 180 mL of ultrapure water and stirred vigorously. After 120 seconds, the pH of the reaction solution was adjusted to 12.0 with 1 M NaOH and subsequently 0.24 mg NaBH₄ was added. The pH of the solution was lowered to 2.5 with 0.3 M HCl after 30 minutes and allowed to react while stirring for 6 hours. Isopropyl alcohol was added at 1 : 1 (v/v) in order to precipitate the AuNCs. The solution was centrifuged at 14 000 rpm in order to collect the AuNCs. Finally, the AuNCs were further washed with methanol.

Extensive *M. thermoacetica* culturing protocols are described in detail in Sakimoto *et al.*¹¹ Briefly, an initial inoculum of *M. thermoacetica* (ATCC 39073) was cultured in 10 mL anaerobic heterotrophic media at 52 °C after slow thawing from –80 °C. The headspace of the 15 mL volume tube was filled with 80 : 20 mixture of N₂ : CO₂ at 150 kPa. After two subsequent rounds of culturing 0.5 mL of 4 mg mL^{–1} Au₂₂(SG)₁₈ was added to each culture tube when OD₆₀₀ = 0.28. After 24 hours, each culture was washed at 2500 rpm for 10 min, and the cell pellet was resuspended in 3.5 mL of autotrophic medium supplemented with 0.1 wt% cysteine and 1% (w/v) sodium alginate.

Encapsulation of photosensitized *Moorella thermoacetica*

As previously described, 1% (w/v) sodium alginate was directly added to the autotrophic media which is used to resuspend the AuNCs-containing bacteria. The microbeads were formed by injecting the alginate solution (5 mL per hour) through a 25G needle parallel to a flowing stream of N₂ gas into 6.5 mL of stirred autotrophic media supplemented with 2% CaCl₂. We then distributed each 10 mL total solution (alginate spheres and liquid autotrophic media) into 25 mL anaerobic tubes, each with 5 mg of TiO₂ anatase nanopowder. In order to promote enzymatic activity, each tube was pressurized with 150 kPa of 80 : 20 H₂ : CO₂ and incubated for 12 hours at 52 °C.

Photosynthesis, measurements and sample characterization

Before the light experiments, the headspace of each sample tube was exchanged with 80 : 20 N₂ : CO₂ and pressurized to 150 kPa. The light intensity of a 75 W xenon lamp (Newport) with an AM 1.5 G filter was calibrated to 0.2% sun. Acetate concentrations were measured by quantitative ¹H-NMR with a sodium 3-

(trimethylsilyl)-2,2',3,3'-tetradeuteriopropionate internal standard. All spectra were processed with MestreNova software. Furthermore, alginate microbeads were imaged with differential interference contrast microscopy using a Zeiss Axioimager upright microscope. Sample preparation for environmental SEM consisted of microtoming individual alginate microspheres with a cryostat (Leica CM3050S). E-SEM was undertaken with an FEI Quanta microscope (Thermo Scientific).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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